Electrochimica Acta, 1969, Vol. 14, pp. 741 to 747. Pergamon Press. Printed in Northern Ireland

DIFFUSIONAL FLOW UNDER NON-ISOTHERMAL LAMINAR FREE CONVECTION—II. EXPERIMENTAL APPROACH*

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Abstract—The rate of a non-isothermal free convection process has been measured at different temperature gradients in an electrochemical cell having parallel vertical plate copper electrodes, the reaction being the electrodeposition of copper from a copper-sulphate–sulphuric-acid solution.

Results agree with the theoretical equation derived previously. They are correlated in a way similar to isothermal free convection in terms of dimensionless ratios, and an equivalence between thermal gradient and rate of stirring under laminar forced convection is established.

Résumé—On a mesuré la vitessed 'un processus à convection naturelle non-isothermique a différents gradients de temperature dans une cellule électrochimique avec des électrodes verticales et parallèles de cuivre, où la réaction étudiée est l'électrodéposition de cuivre dans des solutions de sulfate de cuivre-acide sulfurique.

Les données expérimentales sont en concordance avec l'équation théorique obtenue dans une étude antérieure. Les résultats sont présentés d'une manière analogue à ceux dela convection naturelle isothermique avec emploi des relations adimensionelles. On a établi la relation entre l'effet du gradient thermique et la vitesse d'agitation déduite pour la convection forcée en régime laminaire.

Zusammenfassung—Man bestimmte die Geschwindigkeit eines Prozesses mit nichtisothermer natürlicher Konvektion. Zu diesem Zweck wurde die Kupferabscheidung in einer Zelle mit parallelen senkrechten Elektroden bei verschiedenen Temperaturgradienten untersucht.

Die Ergebnisse bestätigen die früher abgeleitete theoretische Beziehung. Sie können durch eine dimensionslose Korrelation, ähnlich wie fur den isothermen Fall, ausgedrückt werden. Es konnte ein Zusammenhang zwischen dem Temperaturgradienten und der Rührintensität bei erzwungener laminarer Konvektion gefunden werden.

INTRODUCTION

IN PART I of this work,[1] a theoretical solution for the non-linear system of three coupled equations related to the mass transfer under laminar free convection provoked by the simultaneous effect of concentration and temperature gradients was attempted. The resulting mass-transfer equation yields a qualitative interpretation of results recently published.[2] No further test of the equation could be attempted with those results due to the design of the electrochemical cells.

In order to make a quantitative test of the theoretical result and to evaluate the validity of the assumptions made, we have studied an electrochemical system which approaches the ideal conditions required in the theoretical derivation. A cell involving two parallel vertical plate electrodes under simultaneous thermal and concentration gradients has been used. For a cell with such a geometry both the thermal and mass-transfer equations under isothermal conditions are also known.[3–5]

For the purpose of the present work a suitable design of the cell can be obtained from equations derived previously.[1] To evaluate the minimum size of the cell it should

* Manuscript received 13 May 1968.

be taken into account that the distance between the electrodes must be at least twice the distance of the boundary layer. As the boundary layer is mainly determined by the effect of the thermal gradient, the thickness of that layer, δ_0, is obtained by considering the dimensionless variable Λ, which is related to δ_0 by

$$\Lambda = \left(\frac{g\beta}{4\nu^2}\right)^{1/4} \frac{y}{x^{1/4}}, \tag{1}$$

which yields $\Lambda = \Lambda_0$ at $y = \delta_0$. The meaning of the terms in (1) is given in Part I. To obtain the largest value of δ_0, required for cell design, we have taken the largest Λ_0 available which corresponds to the lowest temperature used. Values of δ_0 for different values of x are assembled in Table 1. According to these results we conclude that a cell of relatively small size appears suitable for the purpose.

TABLE 1. DATA CALCULATED WITH EQUATION (1)

$\Lambda_0 = 0{\cdot}820 \quad \nu = 1{\cdot}766 \times 10^{-2}$ cm²/s $\quad y_0 = 0{\cdot}0972 \times x^{1/4}$ cm

x cm	$x^{1/4}$ cm$^{1/4}$	$y_0 \times 10^2$ cm
0·5	0·84	8·16
1·0	1·00	9·72
2·0	1·19	11·6
3·0	1·32	12·8
4·0	1·41	13·7
5·0	1·50	14·6

EXPERIMENTAL TECHNIQUE

The cell was made of three different pieces of Lucite which were assembled and kept in position by metal rods, which passed through the Lucite pieces, provided with washers and nuts. The space containing the electrolyte solution was a cube of about 4 cm side bounded by two Lucite pieces holding the anode and cathode and the central piece, the walls of which were made with thick Lucite, to avoid appreciable heat exchange with the environment. Through the top of the central part, two holes were drilled, one to pour the solution into the cell and the second to insert a reference electrode, when necessary.

The anode of the cell was a vertical copper plate of 16 cm² which formed a complete wall of the cell just in front of the cathode. A 1-cm² copper cathode parallel to the anode and placed from the bottom of the cell upwards was used as the working electrode. Electrodes were stuck to pieces of Lucite, so that the geometry of the cell was that of a parallelpiped with vertical electrodes.

The electrodes were independently thermostated by circulating water through chambers one of whose sides were the non-active side of the electrodes, conveniently isolated with thin varnish layers. Two Ultrathermostats were employed for the purpose. A scheme of the cell is shown in Fig. 1.

Aqueous solutions of copper sulphate (0·005 M) in sulphuric acid (1·5 M) were employed. Each solution was deaerated as usual and the cell was filled avoiding any bubbles being left in it. These solutions proved useful to study mass-transfer phenomena with electrochemical methods. They yield a thin and smooth copper deposit so that the electrode area does not appreciably change during at least five successive determinations.

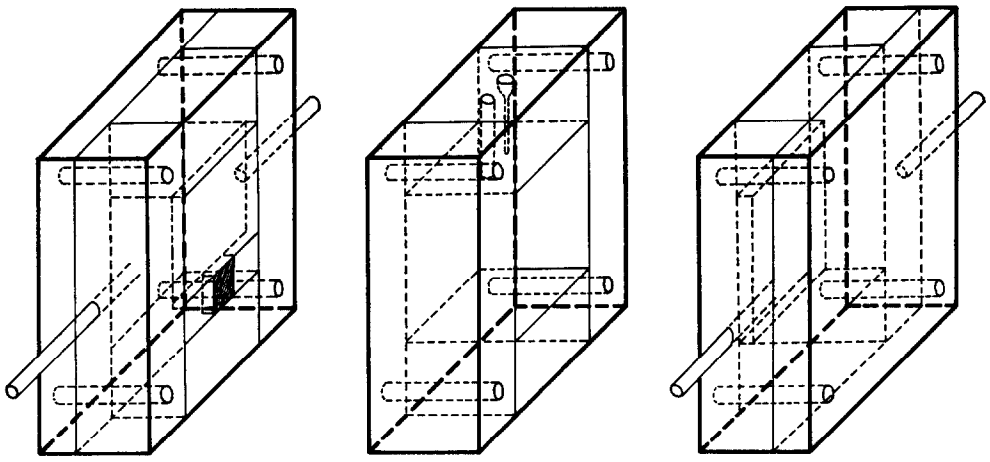

FIG. 1. Scheme of the cell.

Conventional circuitry was employed to obtain the current/voltage curves and to evaluate the corresponding limiting currents.

As the surface area ratio between the anode and the cathode was large, the former was usually employed as reference electrode.

Between successive experiments the electrodes and their frames were polished to a mirror surface with a suspension of fine alumina powder on a flat plate covered with chamois.

Experiments covered a temperature gradient from 0 to 10°C, with mean temperatures from 10 to 40°C. Usually for each solution employed a set of runs was made beginning with the two electrodes at the same temperature, and then the temperature of one electrode was modified while keeping the other at a constant temperature.

The time required to obtain steady readings in the limiting current region depended on the temperature gradient. Thus, when $\Delta T = 0$, about 20 min were required for steady readings, while at ΔT greater than 4°C current stabilization occurred in a few min. In the region of $\Delta T = (\Delta T)_{i=0}$ a definite instability of current was noticed.

RESULTS AND INTERPRETATION

The average rate equation, in terms of limiting current density, i_L, derived for diffusional flow under nonisothermal laminar free convection on a vertical plate working electrode in the presence of a large excess of supporting electrolyte is, as derived before,

$$i_L = 0{\cdot}9zFD_iC_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4} X^{-1/4}, \qquad (2)$$

where α and β are respectively the densification and expansion coefficients as defined.[1] Other symbols have the usual meanings. In deriving (2) a semi-infinite nonisothermal convective diffusion process was assumed, and the temperature gradient was defined as the difference between the temperature at the electrode T and a reference temperature, T_0 at $y = \delta_0$. In applying (2) to the present results it is necessary to fix the significant variables according to the operating conditions. Thus, the reference temperature has been chosen as the mean temperature between the anode and the cathode.

The other variable to be defined is the distance X. When no temperature gradient exists between the electrodes, the boundary layer for convective diffusion under free convection starts at the lower end of the electrode (active surface). When a temperature gradient exists and the temperature is kept constant over all the surface in contact with the solution, two distinct cases arise. In the first case, the origin of the active surface coincides with the origin of the vertical wall; thus both the thermal and diffusion boundary layers start at the same origin and consequently, X is taken as the total height of the electrode. In the second case, when no such coincidence exists, the boundary layers are originated at different sites, so there is a relaxation process, which is not comprised in (2). The present experimental conditions give the first case, so the distance X is the electrode height.

The properties of the solutions were chosen considering the different thickness of the boundary layers in the case of non-isothermal free convection.[1] Thus, the Schmidt number is taken at the working electrode temperature while the Prandlt number is taken at the mean temperature T_m between anode and cathode. This may be not strictly correct as far as average temperatures and properties of solutions are concerned but affords an appreciable simplification in the calculations. The error which this approximation introduces may be considered negligible when compared with the assumptions involved in the theoretical derivation. The values of the diffusion coefficient of copper ion in sulphuric acid solutions D_i, the viscosity, η, the density, ρ, the thermal conductivity, K, and the specific heat at constant pressure, C_p, were taken from the literature.[6–8]

Data assembled in Tables 2–5 correspond to both positive and negative temperature gradients, referred to the temperature of the working electrode, for increasing and decreasing mean temperatures. $(i_L)_t$ is the theoretical limiting cd calculated with (2) and $(i_L)_{e,c}$ the experimental one. The experimental limiting currents were corrected for the residual current, which was a constant affecting both experiments either under isothermal or non-isothermal free convection. As already deduced in the theoretical derivation of (2), the current *vs* temperature-gradient curve exhibits a region located at negative temperature gradients where no steady current flow is obtained. This effect is predicted in the neighbourhood of $(\Delta T)_{j=0}$ where the natural convection effect is cancelled by the density change due to the thermal gradient.

TABLE 2. DATA OBTAINED AT $+\Delta T$ AND AT INCREASING T_m

T_a °C	T_c °C	ΔT °C	$(i_L)_t \times 10^3$ A/cm²	$(i_L)_{e,c} \times 10^3$ A/cm²
26·2	28·9	1·05	0·326	0·375
27·3	36·3	4·50	0·519	0·527
27·3	41·3	6·80	0·653	0·687
27·3	45·4	9·05	0·771	0·789
27·3	48·3	10·5	0·862	0·892
27·3	49·0	10·85	0·886	0·867
27·3	52·6	12·65	1·028	0·957
27·2	32·1	2·45	0·414	0·425
27·2	35·8	4·30	0·510	0·535
27·2	38·8	5·80	0·582	0·645
27·2	42·9	7·85	0·859	0·787
27·2	29·2	0·95	0·322	0·310

TABLE 3. DATA OBTAINED AT $+\Delta T$ AND AT DECREASING T_m

T_a °C	T_c °C	ΔT °C	$(i_L)_t \times 10^3$ A/cm²	$(i_L)_{e,c} \times 10^3$ A/cm²
4·3	27·3	11·5	0·536	0·519
5·7	27·3	10·8	0·522	0·529
8·2	27·3	9·55	0·508	0·520
12·7	27·3	7·30	0·479	0·499
16·0	27·3	5·63	0·452	0·429
20·0	27·3	3·65	0·411	0·403
16·0	27·3	5·63	0·452	0·468
20·0	27·3	3·65	0·411	0·428
24·3	27·3	1·50	0·335	0·373
26·3	27·3	0·50	0·280	0·218
26·7	27·3	0·30	0·259	0·234

TABLE 4. DATA OBTAINED AT $-\Delta T$ AND INCREASING T_m

T_a °C	T_c °C	ΔT °C	$(i_L)_t \times 10^3$ A/cm²	$(i_L)_{e,c} \times 10^3$ A/cm²
40·3	27·2	6·55	0·447	0·471
35·4	27·2	4·10	0·392	0·386
30·4	27·2	1·60	0·294	0·276
30·4	27·2	1·60	0·294	0·265
29·7	27·2	1·25	0·271	0·290
28·6	27·2	0·70	0·216	0·265
46·0	27·2	9·40	0·493	0·580

TABLE 5. DATA OBTAINED AT $-\Delta T$ AND AT DECREASING T_m

T_a °C	T_c °C	ΔT °C	$(i_L)_t \times 10^3$ A/cm²	$(i_L)_{e,c} \times 10^3$ A/cm²
27·3	22·8	2·25	0·297	0·267
27·2	20·1	3·55	0·321	0·327
27·3	17·0	5·15	0·337	0·339
27·2	14·0	6·60	0·342	0·347
27·3	7·5	9·90	0·341	0·357
27·2	23·5	1·75	0·279	0·180*
27·2	24·8	1·20	0·248	0·235*
27·2	25·5	0·85	0·223	0·280*
27·2	26·7	0·25	0·258	0·270
27·2	27·2	0	0·200	0·200

Correlation of results

Experimental results are easily correlated if (2) is rearranged in a dimensionless form, thus,

$$\frac{i_L X}{zFC_0 D_i} = 0{\cdot}9\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4} X^{3/4} Sc^{1/3}. \tag{3}$$

(3) comprises three dimensionless numbers, defined as

$$Sh = \frac{i_L X}{zFC_0 D_i}, \tag{4}$$

$$Sc = \frac{\nu}{D_i} \tag{5}$$

and

$$Gr^* = (\alpha^{3/4} \pm \beta^{3/4} Z^{1/4})^{4/3} \left(\frac{g}{4\nu^2}\right) X^3, \tag{6}$$

where Sh, Sc and Gr^* are respectively the Sherwood, Schmidt and modified Grashof numbers, containing at the same time the dimensionless ratio

$$Z = \frac{Sc}{Pr}. \tag{7}$$

(4)–(7) give with (3)

$$Sh = 0{\cdot}9(Gr^* Sc)^{1/4}, \tag{8}$$

which has the same form as equations already known for isothermal free convection.[4,5]

Figure 2 shows the experimental results plotted according to (8). Those results which show a definite instability were omitted in the correlation plot. The dotted line is the theoretical one with slope of 0·9. The average error of all the determinations referred to the theoretical slope is $A = \pm 0{\cdot}010$ (mean square error, $M = \pm 0{\cdot}014$; probable error, $R = \pm 0{\cdot}009$).

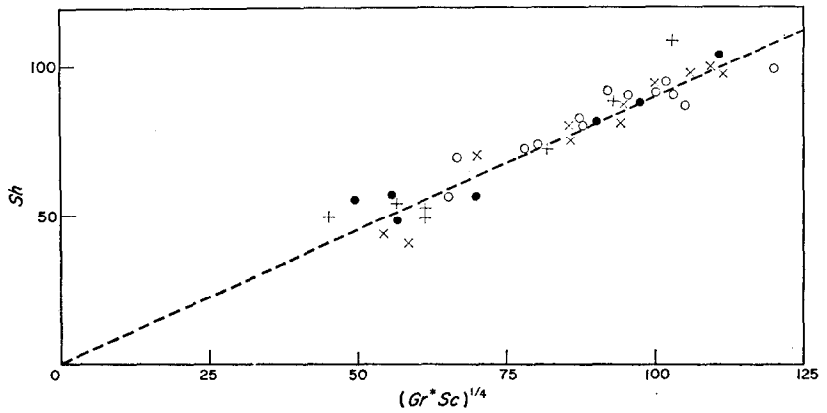

FIG. 2. Plot of equation (8).
○: $+\Delta T$; increasing T_m,
●: $+\Delta T$; decreasing T_m,
+: $-\Delta T$; increasing T_m,
×: $-\Delta T$; decreasing T_m.

Comparison between mass transfer rate increase due to non-isothermal free convection and forced convection under laminar flow

From the viewpoint of the transport process, the thermal gradient provokes an increase in the rate process, comparable to stirring. Let us estimate the equivalence between the thermal gradient and the relative velocity of the solution, assuming that laminar flow prevails. For this case it is necessary to consider a system of simple geometry which has an exact solution of the mass-transfer differential equations, such as the rotating disk electrode, which may be suitable for the purpose.

By equating (2) with the rotating disk electrode rate equation as derived by Levich,[4] we have

$$0{\cdot}62\,\omega^{1/2} = 0{\cdot}90\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{*3/4}}{Pr^{1/4}}\,\Delta T^{3/4}\right)^{1/3}\left(\frac{g}{4}\right)^{1/4} X^{-1/4}, \tag{9}$$

where ω is the rotation speed of the disk electrode in rad/s.

Re-arranging (9) we obtain

$$\Delta T = \frac{Pr^{1/3}}{\beta^*}\left(5{\cdot}2 \times 10^{-3}\omega^{3/2}X^{3/4} - \frac{\alpha^{3/4}}{Sc^{1/4}}\right)^{4/3}. \tag{10}$$

According to (10) for values of

$$5{\cdot}2 \times 10^{-3}\omega^{3/2}X^{3/4} \gg \frac{\alpha^{3/4}}{Sc^{1/4}}, \tag{11}$$

the second term in brackets may be neglected, yielding a quadratic relationship between the temperature gradient and the speed of rotation, which is a measure of the stirring of the system,

$$\Delta T = K'\omega^2, \tag{12}$$

where K' is a proportionality constant involving the distance X, the expansion coefficient, β^*, Prandtl number and the numerical coefficient of (11)

We conclude that under certain circumstances the existence of a thermal gradient superimposed on a cell in which the process is under free convection–diffusion control, provokes an appreciable rate increase. Therefore, in some cases this effect can be employed instead of any stirring.

Acknowledgement—The present work was in part supported by a grant of the Consejo Nacional de Investigaciones Cientificas y Tècnicas of Argentina. S. L. Marchiano, acted as a full-time researcher of the Departmento de Ingeniería Química de la Facultad de Ingeniería de la Universidad Nacional de La Plata.

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